Table III.

$\theta°$.	p.	P.	p/P.
33·9	0·97	3·93	0·24
41·8	1·46	6·04	0·24
52·2	2·15	10·25	0·20
61·0	3·16	15·59	0·20
69·0	4·31	22·34	0·19
77·6	6·36	31·17	0·20
87·8	8·96	48·30	0·18
93·7	11·94	60·39	0·19

The lowest curve is the isohygrometric plotted from the mean ratio of Table III. In this case the agreement of the points with the curve appears remarkably good, considering the experimental difficulties.

Observations and Photographs of Black and Grey Soap Films.

By Herbert Stansfield, B.Sc., Research Fellow of the University of Manchester.

(Communicated by Arthur Schuster, F.R.S. Received January 3,—Read January 25, 1906.)

[Plates 2—3.]

1. Some years ago, while working as a research student, in continuation of Reinold and Rücker's work on soap films, I made measurements on a large number of black films. The conditions of the experiments were not suitable for observing the thinner black, and I did not notice it, although I knew that it had been recorded by Newton, and that Reinold and Rücker* had not only seen the two blacks together, but had also obtained electrical observations indicating that the darker black was half the thickness of the other.

Three years later, Johonnott† published the results of optical measurements of black films, which showed that the thinner black was half the limiting thickness reached by the thicker black in the process of thinning.

On taking up the subject again rather more than a year ago, I wished to become familiar with the thinner black, and with this object examined flat

* 'Phil. Trans.,' A, vol. 184 (1893), p. 513.

† 'Phil. Mag.,' vol. 47 (1899), p. 501.

vertical films, with a low power microscope and reflected light. Using first a solution of potassium oleate in water I failed to observe any sharply defined patches of thinner black, but I found that the films often exhibited several grey tints, sharply separated from one another, and apparently intermediate in thickness between the coloured part and the black. Later, with films formed from a solution of oleate of soda in water, I had no difficulty in observing the thinner black, as it forms in circular patches whose boundaries are sharply marked. With this solution several grey tints were also observed, and it was found that the change from the thicker to the thinner black was the last of a series of similar changes that take place as the film thins.

These grey tints had not, as far as I am aware, been recognised before, although Reinold and Rücker* speak of a grey colour obscuring the boundary between the black and coloured parts of a film, when an electric current was employed to thicken the film.† These new steps in the process of thinning seemed sufficiently important to justify some trouble being taken to obtain photographs, especially as the change from the thicker to the thinner black had not, as far as I know, previously been photographed. Accordingly a special film box and camera were constructed, and the photographs illustrating this paper, showing the stages in the thinning of a sodium oleate film, were obtained in February, 1905.

Since then attention has been drawn to the existence of these new films, by a paper communicated by Johonnott‡ to the American Physical Society.

2. The arrangement of the apparatus for taking the photographs is shown in fig. 1. A is the film box, L a photographic lens of $5\frac{3}{4}$ inches focal

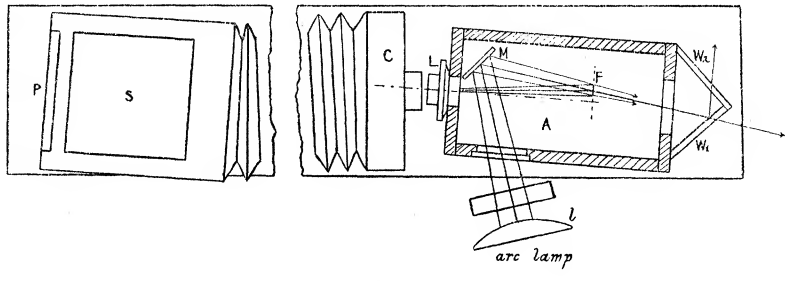


FIG. 1.

length, and C the body of the camera. Light from an arc lamp passes through a condenser and water cell, enters the film box by a plate-glass

* 'Phil. Trans.,' vol. 177 (Part II, 1886), p. 680.

† I find that the grey tints can readily be produced at the boundary by sending an electric current across it from the coloured part into the black.—15.2.06.

‡ Abstract. 'Physical Review,' vol. 20, p. 388, June, 1905.

window, falls on the mirror M and is reflected on to the film at F. The film acting as a plane mirror, reflects some of the light incident upon it into the lens L, and a magnified image of the film is formed at the other end of the camera, which is closed by the plate-holder P.

The main beam of light leaves the film box by the windows W_1 and W_2, which are arranged so that the light they reflect does not go back into the box. The plane of the film must be normal to the axis of the camera lens, if all parts are to be in focus together; the film must also be placed so that the beam of light reflected from it shall enter the lens; and as the incident light comes from one side, it is necessary, in order to fulfil both conditions, to place the film as shown in fig. 1, a little to one side of the axis of the lens.

One advantage of using oblique illumination is that the bright spot where the beam of light falls on the window W_1 is not in the field of view of the photographs.

S, fig. 1, is a horizontal focussing screen in the top of the camera box, and a hinged plate-glass mirror, silvered on the front, is usually placed so that the image is formed on the screen instead of on the photographic plate. The mirror is turned out of the way just before a photograph is taken.

The time of the exposure is regulated by a Bausch and Lomb shutter attached to the camera lens.

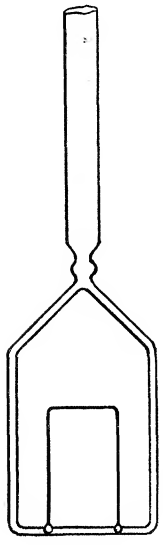


Fig. 2.

In order to prevent too rapid evaporation from the films, the film box is closed up so as to be almost airtight, and water is placed in a shallow tray covering the bottom. A water manometer is employed to test for leaks.

The films are formed on a small frame of thin glass rod, supported and protected by a stronger outer frame, as shown (actual size) in fig. 2. The inner frame is 8 mm. by 15 mm. This type of glass frame was described by Johonnott* in connection with his interferometer measurements of black films. I employed the method he describes for bending the glass rod into shape.

To make a film, the glass rod handle is pushed down until the inner frame is immersed in the soap solution in a short test tube standing on the bottom of the film box; it is then pulled up again until the frame is quite out of the solution; there is, however, always a line of liquid along the bottom of the films.

3. The photographs numbered from 1 to 4, Plate 2, show stages in the thinning of a film made from a solution of oleate of soda in

* 'Phil. Mag.,' vol. 47, p. 501.

water, 1/60. The film thinned rapidly, and only lasted five minutes, breaking soon after the change from the thicker to the thinner black had taken place. The exposure in each case was a fifth of a second.

In No. 1, the dark area in the middle of the film at the top is the thinnest of the greys; the next thicker one can be seen at each side; and, in the original, it is possible to distinguish a third, still thicker, stretching across the film below the other two. The lower edge of the thinnest grey area is pulled up in two places by fine filaments stretching across to some thicker material in contact with the glass frame. The horizontal dark bands in the photograph, lower down the film, indicate the positions of the red bands of the 1st, 2nd, and 3rd orders; the first dark band is much darker than the other two.

Close to the sides of all the photographs in this plate there are indications of the upward flow of parts of the film that have been thinned in consequence of their proximity to the glass frame.

No. 2 was taken as soon as possible after the appearance of black spots in the thinnest grey; small white specks have been formed on the advancing edges of the black areas, and they have been carried, by their weight, towards the lowest parts of the edges.

No. 3 shows the stage when the black areas have all joined together, and formed a band right across the film. The three grey films can still be traced, like a flight of steps leading down to the black; the last two steps are much clearer than the first.* Some of the white specks, or discs, have become so heavy that they have dragged down the edges on which they were formed, and have come into contact with lower edges; there they have taken up further material, until they have become circular lens-shaped thickenings, heavy enough to break away from the edges. They are seen falling down the film, leaving streaks of reduced thickness behind them.

No. 4 was taken soon after the thicker black, seen in No. 3, began to change into the thinner black. The area of thinner black spread rapidly, and a heavy crop of white discs formed on the edge.

No. 5, Plate 3, was taken a few minutes before the preceding photographs, on another film; it was accidentally given an exposure of one or two seconds, instead of a fifth of a second, so the white discs on the boundary

* *Note added February* 15.—The existence of narrow bands of grey, as shown in this photograph, would explain the bending of the interference fringes near the edge of the black sometimes observed by Reinold and Rücker ('Phil. Trans.,' II, 1883, p. 656), when they were making optical measurements of the thickness of black films. They found it necessary to assume that the black films increased in thickness near the boundary, and they calculated the thickness required to produce the displacement of the fringes observed.

between the two blacks have moved some distance, and increased in size during the exposure. It may also be noticed that the upper edge has moved further than the lower edge, this is probably due to the whole patch of thinner black rising though the surrounding thicker black. The unusually long exposure has helped to show clearly the variations in thickness of the thicker black. There are two filaments stretching down from the top of the film, across the band of thicker black, to two projections on the upper edge of the coloured part of the film. They are too fine to be visible in this plate, but their directions can be traced in the original negative.

No. 6 is a photograph of a sodium oleate film in an advanced stage of thinning, showing the grey pattern that is often formed. Almost all the coloured part of the film has gone, and the black has all changed to thinner black. The mottled parts in the middle of the film at the bottom, and supporting the grey pattern on the right, consist of collections of nodules that have formed during the thinning of the film.

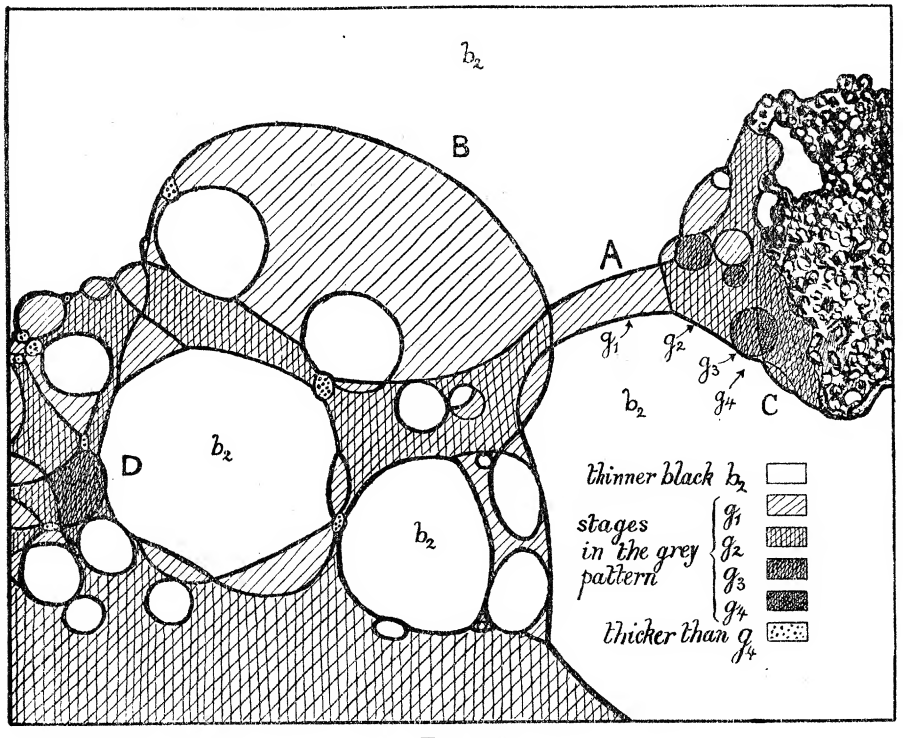


FIG. 3.

Fig. 3 is a drawing of part of the negative enlarged about three times, or rather more than 20 times the actual film, in order to show the details of the

pattern. The thinnest grey and the thinnest but one, marked g_1 and g_2, make up most of the pattern; but there are several small patches of a third grey, and part of a circular patch on the right, marked g_4, is clearly a still thicker stage.

At first sight a grey pattern often suggests that some of the thickenings are produced by the overlapping of two layers. For example, the appearance of fig. 3 suggests that the arch of first grey A stretches across the rounded area B, thickening it up to the second grey, where they overlap; and the curved edge of the patch C appears to overlap the circular patch producing the fourth grey. The impression of overlapping is, however, not supported by watching the movements of the grey pattern. If the grey films are built up of numbers of layers, the layers appear to be unable to move across one another. I have noticed nothing in the movements of the grey pattern more suggestive of stratified structure than the apparent removal of successive layers in the thinning process represented in Plate 2.

No. 7 is a photograph of a film made from a solution of potassium oleate in water, 1/60. The film was seven hours old when this photograph was taken, and, instead of thinning in the usual way, it had deposited a large amount of solid material, which is seen on the left-hand side of the film attached to the glass frame. I found that the film box was leaking badly, owing to a cemented joint along the edge of one of the windows having cracked, and this may have been the cause of the unusually large deposit of solid material.

No. 8 is a photograph of a film made from a solution of sodium oleate in water, 1/60, mixed with 40 per cent. of its volume of Price's glycerine.

It is difficult to recognise the two blacks with this solution. Large numbers of small specks are visible falling through the black; on entering the coloured part of the film they soon become considerably larger, and a number of them may be seen falling in a shower a little to the left of the centre of the film.

4. I made a number of experiments with films formed in a small airtight glass cell that could be immersed in a water bath with plate-glass sides, and kept at high or low temperatures, in order to find out whether the temperature affected the behaviour of the films. I particularly wished to try whether changing the temperature would cause the sodium oleate films to lose, or the potassium oleate films to gain, the property of changing abruptly from the thicker to the thinner black.

I did not find any differences in the behaviour of either the sodium or potassium oleate films over the range of temperature tested, which extended from 10° C. to 35° C.

These experiments showed that the hygrometric conditions are far more important than the general temperature. A film in the thicker black condition will change to the thinner black if it is allowed to lose water by evaporation, and will thicken up again if the conditions are altered so that the air becomes saturated with moisture, whether the temperature is high or low.

The thicker black is the stage to which the sodium oleate films thin when they are left shut up in a flask, or an airtight glass cell, containing some of the soap solution. If they are warmed by the heat from a source of light they are liable to change into the thinner black. I often bring about the change by focussing the beam of light from the arc lamp on to the film. The thinner black will sometimes thicken up again if the light is stopped, and it may be assisted by allowing the beam to fall on the solution instead of on the film.

If the film is thickened rapidly, the change takes place by the formation of large numbers of small circular discs of the thicker black, which, increasing in size, and falling down the film like a shower of snow-flakes, pile higher and higher, and join together, until all the thinner black is filled up.

5. The white discs that are formed on the retreating edge of the thicker black, when the thinner black is being formed, may represent the material that is removed from the thicker black in reducing its thickness; they must be produced from the thicker black, and they give some evidence as to the material of which it is formed. The discs formed are much smaller when the area of thinner black extends slowly, and in some cases only a faint stream of misty thicker material is seen falling away from the bottom of a patch of the thinner black, as it rises through the surrounding thicker black.

The thinner black often develops numbers of minute brown discs or grains soon after its formation; they appear brown in comparison with the bluish light reflected by the film. With oblique illumination they shine as bright specks on the dark background.

The light scattered by these grains causes the black part of a film, viewed by transmitted light, to look more like a solid membrane than a liquid film.

The circular lens-shaped thickenings falling through the film in photographs Nos. 3 and 4, Plate 2, are formed out of the material collected during the thinning process, as discs and irregular thickenings on the various retreating edges. In No. 5, Plate 3, part of the edge of the black has been so heavily weighted with lens-shaped thickenings that it has gone down

with them, drawing out a narrow creek of black; several small patches of black, that have also been taken down, are acting as floats.

In photographs Nos. 7 and 8, Plate 3, the lens-shaped thickenings are seen falling in much larger numbers than in Nos. 3 or 4, Plate 2, because their formation is being assisted by the continual supply of numbers of the small specks or grains that are formed in the black. These grains when they enter the coloured part of the film act as nuclei around which the lens-shaped thickenings form.

When solid material is growing in a film as shown in photograph No. 7, Plate 3, the brown specks or grains in the black can be seen shooting into the tips of the dendritic growth that projects into it. The solid material in contact with the thicker parts of the film appears to grow by catching the lens-shaped thickenings that come near to it, and perhaps also by more continuous absorption from the edge of the coloured film. The edges of a coloured film close to the frame generally become thinner than the neighbouring parts that are unaffected by it, as though the frame withdrew material from the film; and all the edge of the coloured part of the film in contact with the solid material growing in No. 7 is reduced in thickness to the first order white or yellow.

The lens-shaped thickenings are drawn towards the boundaries of the film, in the same way that bubbles floating on the surface of a liquid are drawn to the sides of the containing vessel. They generally shoot into the sides, or cross the boundary of the film into the line of liquid at the bottom; but sometimes they accumulate near the bottom of a film, and in the last stages of thinning form the collections of nodules seen in photograph No. 6.

I am inclined to think that the brown specks or grains that form in the black, and the lens-shaped thickenings, contain a much larger proportion of soap than the original soap solution; and that they consist of a soap jelly which becomes, perhaps, after some further loss of water by evaporation, stiff enough to build up the dendritic structures that sometimes grow in the films.

A film in the condition represented in photograph No. 7, Plate 3, appears to illustrate the explanation of the process of churning given by A. Pockels;* the separation of the soap in the soap film being analogous to the separation of the butter in the bubbles formed in the operation of churning.

The concentration of soap in the surface of a soap solution is a source of inconvenience in forming films. If a frame is cautiously immersed in a solution standing in a bottle, so as to disturb the surface as little as possible, and taken out again so as to lift a film from the surface, the film obtained will be

* 'Ann. d. Physik,' vol. 8, 4, p. 854, July, 1902.

impeded with thickenings from the first, and would be unsuitable for showing the regular formation of the greys and blacks. It is necessary first, in order to obtain a clean film free from thickenings, to break up the surface by jerking the frame out of the solution a few times. This precaution was taken in forming the film on which the photographs Nos. 1 to 4, Plate 2, were taken; No. 5, Plate 3, taken a few minutes before, shows a considerable amount of thick material in contact with the frame at the top, because this precaution was not sufficiently attended to.*

6. A sodium oleate film that is thinning fairly rapidly generally begins to form a grey pattern when it has developed a broad band of the thinner black across the top, and a number of lens-shaped thickenings have been formed on the upper edge of the coloured part of the field. It often happens that part of the edge in the middle of the film goes down with the thickenings on it, drawing out a narrow creek of black as in No. 5. The grey films are then first seen in the creek; they are carried up by rising patches of black and drawn out into bands, which arch over from one side of the mouth of the creek to the other, and often become very long and narrow before they break and allow the patch of black they enclose to escape. The bands of grey appear to be produced in some way from the thickenings on the sides of the creek.

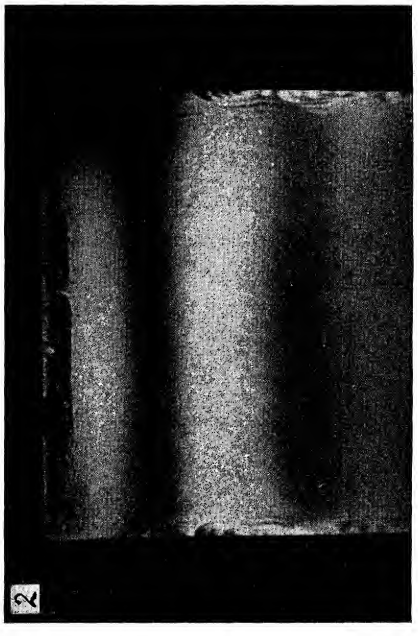
A grey pattern may also be formed under conditions such that all the black is in the thicker state. If the conditions are changed, by warming the film, so that the black thins gradually and then changes to the thinner black, the stages of the grey pattern may also undergo some slight changes and a fresh pattern be developed under the new conditions.

The stages that make up the grey pattern do not appear to be very closely connected with the grey stages formed during the early thinning process.

The thinnest grey in the grey pattern, formed under conditions such that all the black is being rapidly reduced to the thinner black, is not identical with the thicker black. I have seen the thinnest grey of the grey pattern in contact with areas of thicker black which were rapidly shrinking up with white specks or discs on their retreating edges. The thinnest grey was not quite so dark as the thicker black in contact with it, and did not develop white specks on its edge or appear to be affected in any way by conditions which caused the thicker black to disappear very rapidly.

I have only observed three grey stages during the thinning process of sodium oleate films, but I have counted as many as six stages in the grey patterns of these films.

* The formation of solid pellicles on the surfaces of aqueous solutions of soaps and other substances has been described by Ramsden ('Roy. Soc. Proc.,' vol. 72, p. 156).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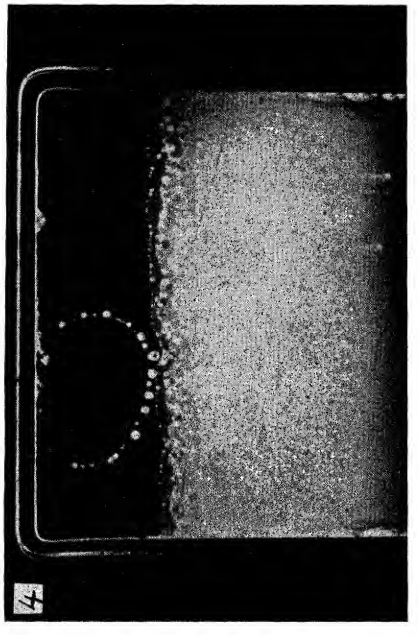
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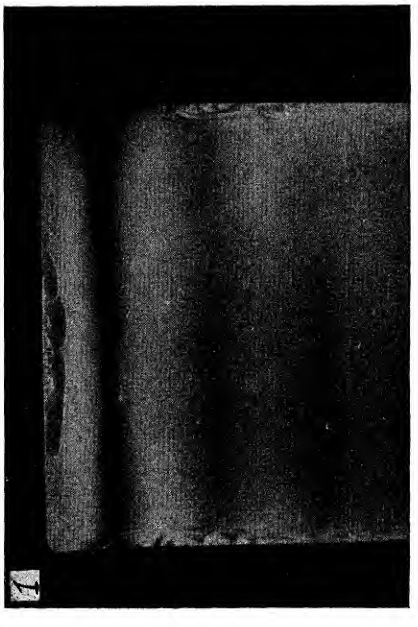
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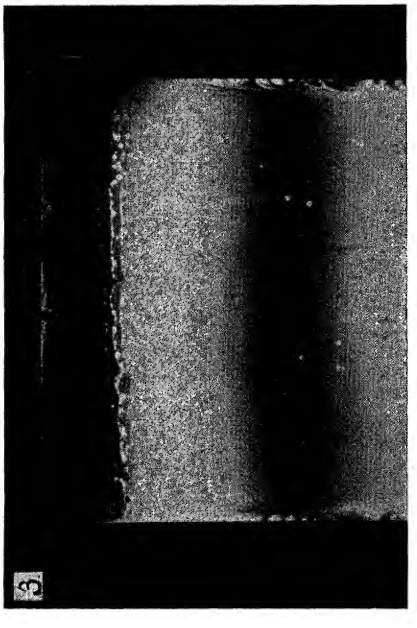
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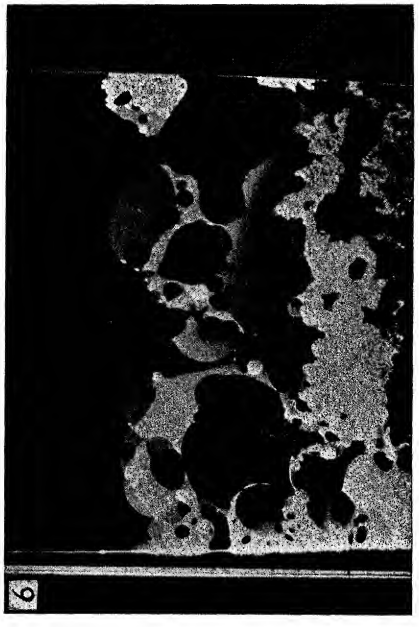
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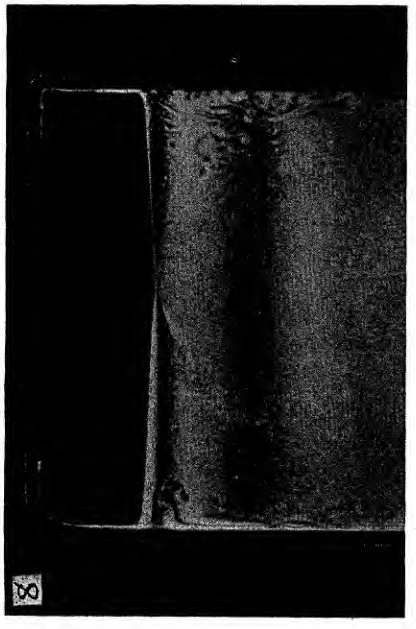
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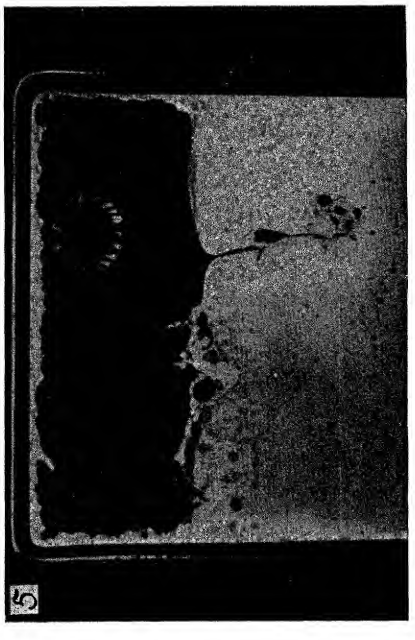
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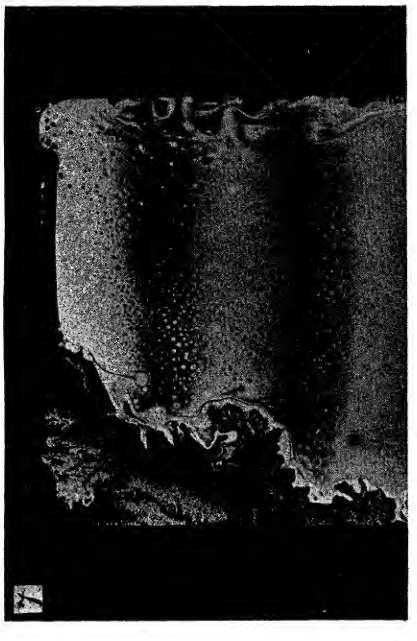
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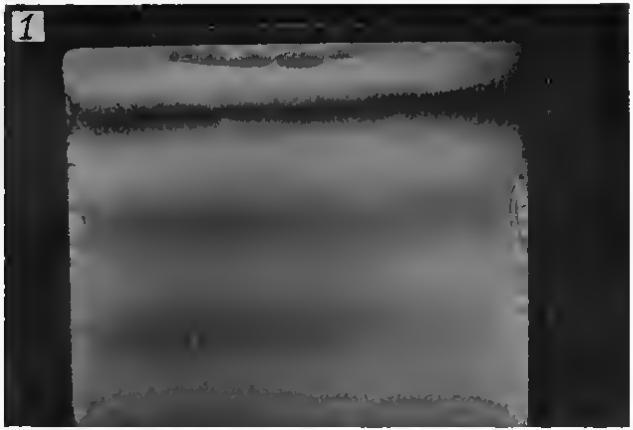
The stages of the grey pattern, even when they are formed under the most trying hygrometric conditions, do not show the tendency to become thinner, by breaking down into the next thinner stage, that is characteristic of the greys formed during the thinning process.

I think the evidence points to the conclusion that the grey pattern does not part with water so readily as the thicker black or the grey films formed during the thinning process.

Perhaps the explanation suggested for the lens-shaped thickenings may also be applied to the grey pattern which appears to be derived from them. The grey pattern may be formed of material that is richer in soap than the material forming the thicker black or the three grey films formed in the thinning process and may on that account not be so readily reduced in thickness by evaporation.

7. In distinguishing the three grey films formed in the thinning process, or the stages in the grey pattern, by numbers, I have called the thinnest stage number one, as the thinner stages form in relatively large areas, and are easily recognised. The plan of calling the thicker films by the higher numbers, corresponds with the numbering of Newton's orders of colours, and with the names β_1 and β_2 employed by Reinold and Rücker for the thinner and thicker black; it is, however, opposed to the method adopted by Johonnott, who speaks of the first and second black according to the order in which they are formed in the process of thinning. I find the names first and second black as used by Johonnott convenient, but have used the terms thicker and thinner black in this paper, in order to avoid any uncertainty.

In conclusion I wish to express my thanks to Professor Schuster for placing the resources of the physical laboratory at my disposal; and to Mr. F. H. Gravely for help in taking some of the photographs.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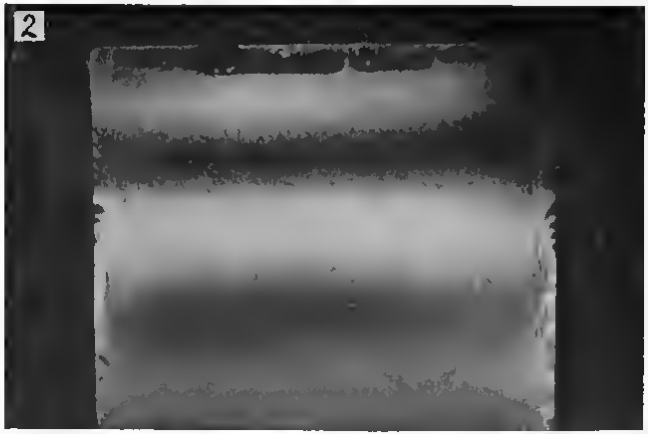
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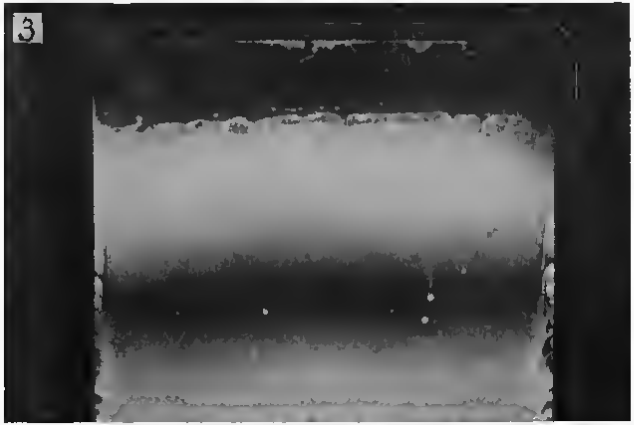
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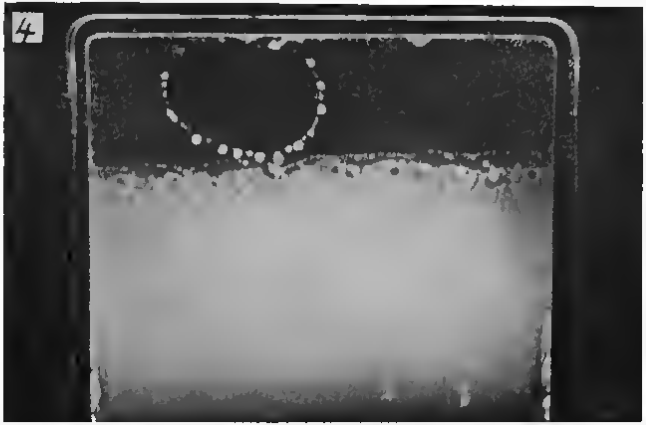
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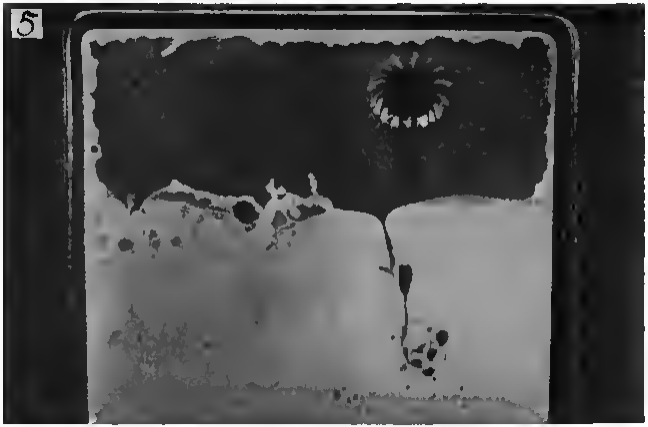
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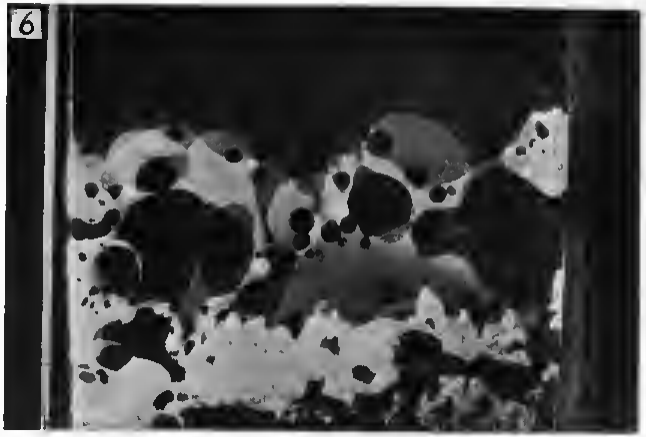
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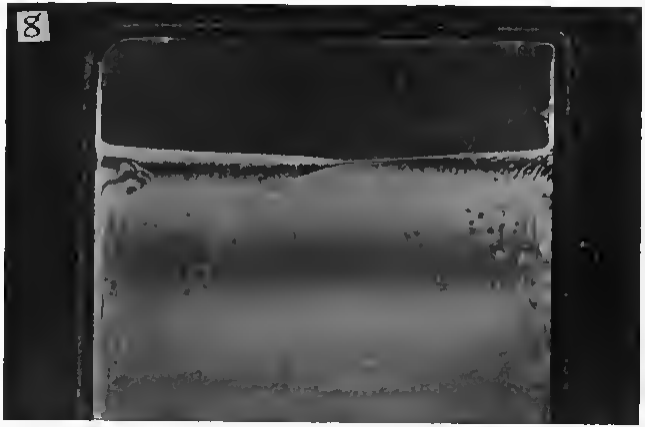
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